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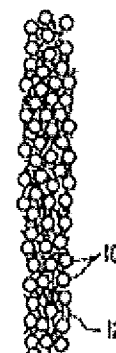
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(54) LITHIUM ION SECONDARY BATTERY AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium ion secondary battery having improved charge and discharge cycle life and manufacture thereof.

SOLUTION: Polyolefin powder grains 10, having melting point of 200°C or less and consisting of PE(polyethylene) or PP(polypropylene); and polymeric powders 12, such as PVDE-HFP having swelling properties by impregnation of an electrolyte are mixed with each other uniformly, a sheet of 10 to 100 microns in thickness is formed to make a separator. An electrolyte is impregnated in polymeric powders 12 after the separator has been formed. Such a separator is various in passing through direction of a lithium ion and disperses uniformly throughout the separator, and thus the occurrence of a local heavy current can be prevented.



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## CLAIMS

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[Claim(s)]

[Claim 1]A lithium ion secondary battery having the separator which polyolefine with a melting point of 200 \*\* or less and polymer holding an electrolyte are distributing uniformly.

[Claim 2]A manufacturing method of a lithium ion secondary battery characterized by comprising the following.

A process with which particle diameter mixes uniformly a polymer particle in which the melting point holds polyolefine particles and an electrolyte of 200 \*\* or less at 100 micrometers or less.

A process of forming a 10-100-micrometer-thick sheet using this mixture, and a process that said sheet is impregnated in an electrolysis solution.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a lithium ion secondary battery whose charge-and-discharge cycle life improved, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]Conventionally, in order to use a lithium ion secondary battery for a various application, it is requested that the cycle life is raised. For example, by making the gel electrolyte which impregnated with the electrolyte between the anode and the negative electrode placed between JP,H4-112460,A, the deposit of a dendrite is prevented and the art of raising a cycle life is indicated.

[0003]The structure where the polymer which held the electrolyte to both sides of the MAIKUROPORASU polyolefin sheet was allotted to JP,H9-22726,A is indicated. Since according to this the penetration of a lithium ion is barred by fusion of polyolefine in the case of misuse and a cell function is suspended, it is supposed that safety will be secured.

[0004]

[Problem(s) to be Solved by the Invention]However, in the thing between which the gel electrolyte which impregnated with the electrolyte between the anode and the negative electrode among the above-mentioned conventional technologies was made to be placed, this gel electrolyte mobilized at the elevated temperature, and there was a problem that an anode and a negative electrode will short-circuit.

[0005]When a MAIKUROPORASU polyolefin sheet was used, there was possibility of generation of a dendrite in the porous part of polyolefine, and there was a problem that an anode and a negative electrode will short-circuit.

[0006]Therefore, in any case, a cycle life was not able to be raised enough.

[0007]this invention is made in view of above-mentioned conventional SUBJECT, and comes out. The purpose is to provide a lithium ion secondary battery whose cycle life improved, and a manufacturing method for the same.

[0008]

[Means for Solving the Problem]To achieve the above objects, it has the separator which this invention is a lithium ion secondary battery, and polyolefine with a melting point of 200 \*\* or less and polymer holding an electrolyte are distributing uniformly.

[0009]A process with which it is a manufacturing method of the above-mentioned lithium ion secondary battery, and particle diameter mixes uniformly a polymer particle in which the melting point holds polyolefine particles and an electrolyte of 200 \*\* or less by 100 micrometers or less, It has a process of forming a 10-100-micrometer-thick sheet using this mixture, and the process that this sheet is impregnated in an electrolysis solution.

[0010]

[Embodiment of the Invention]Hereafter, an embodiment of the invention (henceforth an embodiment) is described according to Drawings.

[0011]The example of the separator used for the lithium ion secondary battery concerning this invention is shown in drawing 1. In drawing 1, the separator has structure uniformly mixed with the polymer particle 12 which has the character in which PVDF-HFP, PAN, etc. contain an electrolysis solution and polyethylene (PE) or the polyolefine particles 10 like polypropylene (PP) swell.

[0012]The polyolefine particles 10 have the particle diameter of 100 micrometers or less. Above-mentioned PE in which it is desirable as construction material for the melting point to be 200 \*\* or less, or the particles of PP are preferred. Not only particle state as shown in a figure but the thing it is supposed that it is fibrous is possible for the polyolefine particles 10.

[0013]PVDF-HFP etc. are used as the polymer particle 12. These are resin which will swell if it impregnates with an electrolysis solution.

[0014]These polyolefine particles 10 and polymer particles 12 are mixed, a 10-100-micrometer-thick sheet is formed, and it is considered as a separator. In the polymer particle 12, the mixing ratio of the polyolefine particles 10 and the polymer particle 12 is in the state where it impregnated with the electrolysis solution, and polyolefine particle:polymer particle (\*\*\*\*\*) =2:8 - 7:3 are preferred for it. Such a separator mixes the polyolefine particles 10 and the polymer particle 12 uniformly first, produces the sheet of the above-mentioned thickness from this mixture, and manufactures it by impregnating this in an electrolysis solution.

[0015]Even if the separator of the lithium ion secondary battery concerning this invention constituted as mentioned above carries out charge and discharge by high electric current, it does not have generation of a dendrite and can prevent the short circuit by this. This is considered to be based on the following Reasons.

[0016]As the conventional separator is shown in drawing 2, much fine pores 16 are formed in the substrate 14. The lithium ion passes these fine pores 16. However, in the conventional separator shown in drawing 2, the lithium ion passes only the fine pores 16 provided in the substrate 14 by fixed density. Therefore, the potential difference by the side of both sides of a separator will be produced in the portion of these fine pores 16. That is, when a big charge and discharge current is sent through a lithium ion secondary battery, a lithium ion moves only in the portion of these fine

pores 16, and big current flows into this portion locally. For this reason, the potential in the outlet side of the fine pores 16 which a lithium ion passes may fall greatly locally, and may fall to lithium potential. If the potential here falls to lithium potential, a lithium ion serves as metal lithium, and this will progress and it will serve as a dendrite. The short circuit of a separator arises inside a lithium ion secondary battery by this dendrite.

[0017]On the other hand, in the separator concerning this invention shown in drawing 1, a lithium ion can move comparatively freely the portion with which between [ 12 ] the polyolefine particles 10 (i.e., a polymer particle) was filled up. And compared with the example shown in drawing 2, various directions are possible for this move direction. Therefore, big current can be prevented from flowing locally also when a big charge and discharge current is sent. That is, in this invention, it means distributing uniformly the fine pores 16 shown in drawing 2 to the whole separator, for this reason, equalization of the current density in a separator could be attained, and big current can be prevented from flowing locally. For this reason, by the downstream of the separator at the time of a lithium ion moving, potential could not fall to lithium potential and generating of a dendrite can be prevented.

[0018]In the separator shown in drawing 1, as the polyolefine particles 10, since PE and PP of 200 \*\* or less are used, the melting point, Even when the rise of local current density arises and temperature rises locally in a lithium ion secondary battery temporarily, these polyolefine particles 10 fuse and the eye of a separator is packed. As a result, movement of the lithium ion in that portion is suspended. The rise of local current density can be controlled by this, and a shutdown function is exhibited.

[0019]Hereafter, the example of the separator of the lithium ion secondary battery concerning this invention is explained as working example.

[0020]PE8.5g with a working example . mean particle diameter of 10 micrometers, PVDF-HFP 1.5g, and THF20g were mixed at 50 \*\* for 1 hour, and it cooled to the room temperature after that. Next, the thin film was formed with the doctor blade method, and it was made to dry at 80 \*\*. This obtained the 30-micrometer-thick separator.

[0021] $\text{LiMn}_2\text{O}_4$  was used as an anode, metal lithium was used as a negative electrode, and the placed opposite was carried out via the above-mentioned separator. This was immersed in the electrolysis solution of  $1\text{molLiBF}_4\text{-EC:DEC=1:1}$ , and the lithium ion secondary battery was produced. The above-mentioned anode adds carbon black 10% to  $\text{LiMn}_2\text{O}_4$ , it is stirred in N-methyl pyrrolidone (NMP) for 10 minutes, and it uses it as positive electrode paste, and is formed from this positive electrode paste. As for this anode, since carbon black was not distributed enough, unevenness of an average of 100 micrometers and a maximum of 300 micrometers existed. Charging current was made to increase using the anode which has this unevenness, and the electrical property was investigated.

[0022]The conventional porous membrane and PVDF-HFP of PE nature were evaluated as a comparative example in accordance with the separator constituted only from a polymer particle swollen with the electrolysis solution.

[0023]When charging current was made to increase, in the case of the cell formed by the porous membrane of PE, the short circuit occurred in the current value of 5C. With the separator swollen with the electrolysis solution, the short circuit generated PVDF-HFP with the current value of 8C. On the other hand, in the separator concerning this invention mentioned above, the short circuit was not generated with the current value of 20C, either.

[0024]In the separator which swelled PVDF-HFP with the electrolysis solution, if there is no shutdown function since a lithium ion is passed from the first, and also temperature becomes high by the rise of local current density, the short circuit of electrodes will occur by mobilization of gel. For this reason, it is thought that a short circuit occurs with small current compared with this invention.

[0025]

[Effect of the Invention]According to this invention, as explained above, since polyolefine particles and a polymer particle are mixed uniformly and equalization of current density is attained, local high electric current can be prevented and generating of a dendrite can be controlled. As a result, the charge-and-discharge cycle life was able to be raised.

[0026]Since it has a shutdown function which polyolefine particles fuse and controls passage of a lithium ion by the rise of temperature also when current density rises locally, failure by a local high current can be prevented.

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